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Cyclobutadiene nickel complex as a catalyst for CH-activation reactions: computational study

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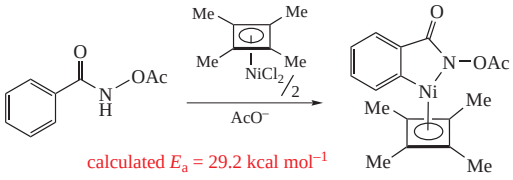
DFT calculations suggest that, similarly to the classical $[CpRhCl_2]_2$ catalyst, the isolobal cyclobutadiene nickel complex $[(C_4Me_4)NiCl_2]_2$ can promote CH-activation of arenes (activation barrier is about 30 kcal mol^{-1}).



Catalytic CH-activation with chelate assistance of directing groups has attracted enormous attention during the last decade.[1] Most of research on this topic has been done with noble metal catalysts, especially with $[(p\text{-cymene})RuCl_2]_2$ and $[Cp^*RhCl_2]_2$ (Figure 1).[2] Despite their success, there is a general initiative to replace these catalysts with derivatives of cheaper and non-toxic 3*d* metals. In particular, it has been found that cyclopentadienyl cobalt complex $[Cp^*CoCl_2]_2$ and its derivatives can be employed.[3] In addition, a limited number of nickel-catalyzed CH-activation reactions have been reported.[4,5] However, the latter typically proceed in the presence of nickel salts as catalysts and therefore require the presence of additional chelate groups in substrates (*e.g.*, 8-aminoquinoline).

In continuation of our recent studies on CH-activation,[6] we envisaged that the cyclobutadiene nickel complex $[Cb^*NiCl_2]_2$ ($Cb^* = C_4Me_4$), which is isolobal to $[Cp^*CoCl_2]_2$, $[Cp^*RhCl_2]_2$, and $[(p\text{-cymene})RuCl_2]_2$, may act as a catalyst in such reactions. Although cyclobutadiene complexes of transition metals are known for more than 50 years,[7] they have been only recently employed in catalysis.[8] Nickel complex $[Cb^*NiCl_2]_2$ has been first synthesized in 1959, but its chemistry has been mostly abandoned for more than 20 years,[9] apparently because its synthesis[10] requires the use of special precursors, namely, toxic $Ni(CO)_4$ with 3,4-dichlorotetramethylcyclobut-1-ene.[11] In view of these difficulties, before experimental work we decided to explore a possible catalytic activity of $[Cb^*NiCl_2]_2$ by DFT calculations.

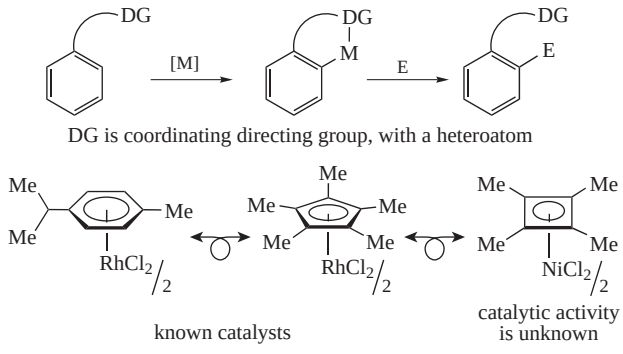
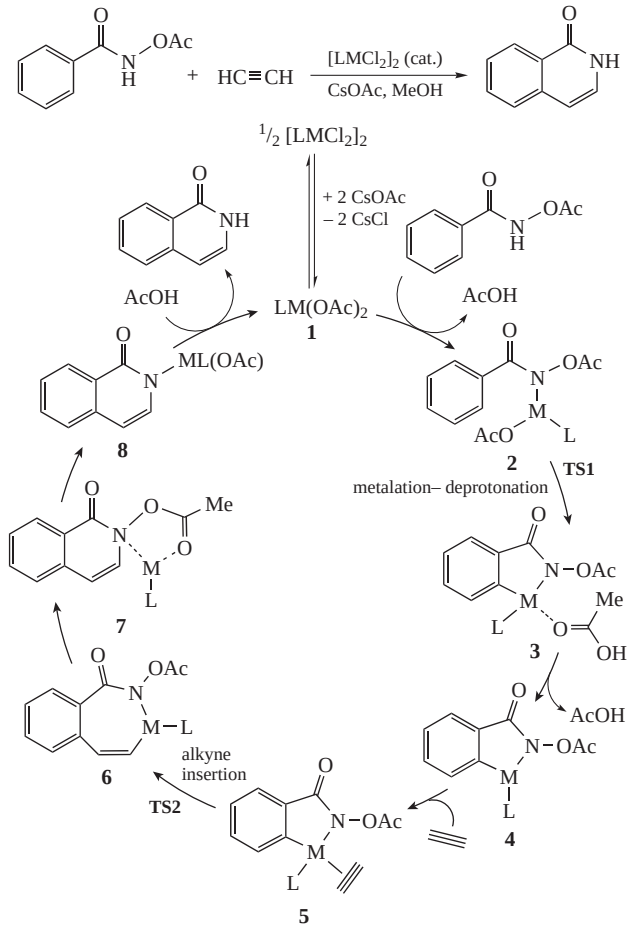


Figure 1 General scheme of CH-activation reaction and possible catalysts.

We considered a model reaction of *N*-acetoxybenzamide with acetylene (Scheme 1). Mechanism of this reaction was studied previously both experimentally and computationally for the $[CpRhCl_2]_2$ catalyst.[12,13] Two key steps have been identified: the concerted metalation–deprotonation (CMD, **2** → **3** *via* $\mathbf{TS1_{Rh}}$) and the insertion of alkyne (**5** → **6** *via* $\mathbf{TS2_{Rh}}$). The calculated



Scheme 1

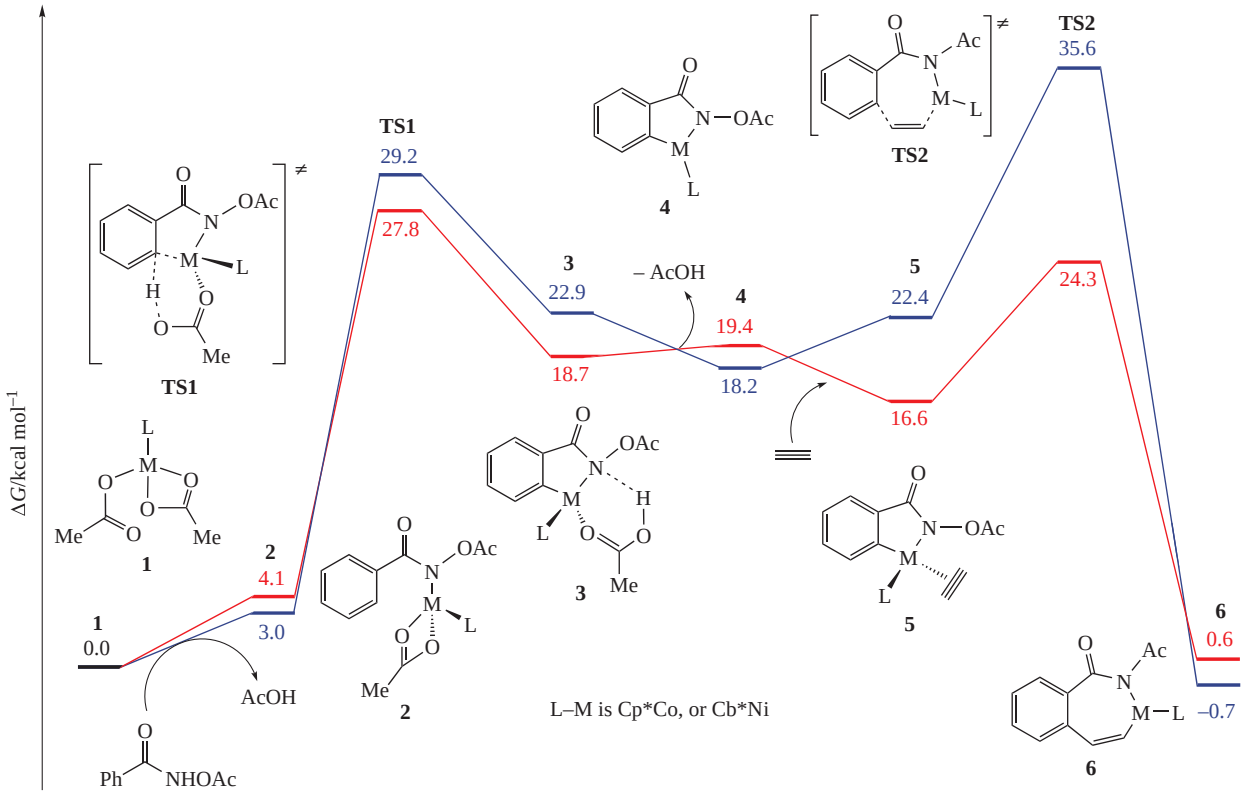


Figure 2 Free energy profile for annulation reaction catalyzed by Cb*Ni(OAc)$_2$ (in blue) and Cp*Co(OAc)$_2$ (in red).

energies of these transition states were 20.5 and 11.4 kcal mol^{-1}, respectively. The relatively low barriers correlate with reasonably fast reaction at room temperature, and the higher barrier of the first stage is in accordance with 15 times slower reaction of deuterium derivative of *N*-acetoxybenzamide (deuterium kinetic isotope effect).

We calculated the main transition states of the catalytic cycle shown in Scheme 1 for [Cb*NiCl$_2$]$_2$ and [Cp*CoCl$_2$]$_2$ catalysts at M06L/TZVP level with SMD correction for methanol solvation (Figure 2). Reductive elimination steps **6** → **8** were not considered because they typically have much lower barriers that are difficult to locate computationally. The M06L/TZVP method was chosen, because it provides a good estimate for organometallic thermochemistry with less than 1 kcal mol^{-1} average deviation from the experimental data.[14] As for the rhodium catalyst, it was assumed that the initial complexes [LMCl$_2$]$_2$ react with CsOAc to give the acetate species LM(OAc)$_2$ (LM is CpRh, Cp*Co, or Cb*Ni). For the cobalt catalyst [Cp*CoCl$_2$]$_2$, the mechanism was qualitatively similar to that for the rhodium species [CpRhCl$_2$]$_2$.[12] However, the energy barriers for the cobalt-catalyzed reaction were higher, namely, 27.8 and 24.3 kcal mol^{-1} for $\mathbf{TS1_{Co}}$ and $\mathbf{TS2_{Co}}$, respectively. This is consistent with experimental observation of generally higher temperatures required for cobalt-catalyzed CH-activation reactions.[3] Note, however, that the related experimental reaction of *N*-chlorobenzamide with alkynes has been reported to proceed even at room temperature,[15] apparently being facilitated by trifluoroethanol solvent.[16]

The calculated profile of the Cb*Ni-catalyzed reaction was found to be notably different from those of CpRh and Cp*Co analogues. While the C–H activation step $\mathbf{TS1_{Ni}}$ has activation energy of 29.2 kcal mol^{-1} (only 1.4 kcal mol^{-1} higher than that of Cp*Co), the insertion of alkyne *via* $\mathbf{TS2_{Ni}}$ has a prohibitively high barrier of 35.6 kcal mol^{-1}. The reason for this is not clear, although it can be tentatively assigned to the higher stability of square planar configuration of nickel in the intermediate **4**. Interestingly, the recent[17] DFT calculations of the similar reaction catalyzed by (Ph$_3$P)Ni(OAc)$_2$ have produced 24.6 kcal mol^{-1} barrier for the C–H activation step and 31.9 kcal mol^{-1} barrier for the alkyne insertion, which are close to those found in this work. This reaction experimentally proceeds at 160 °C.[18]

The detailed analysis revealed the significant deformations of the cyclobutadiene ligand in some of the structures (Figure 3). In particular, the C–C bonds of the cyclobutadiene in the 18-electron piano-stool complexes, such as $\mathbf{1_{Ni}}$, have very close lengths (1.441–1.462 Å). At the same time, the 16-electron structures, such as intermediate $\mathbf{4_{Ni}}$, have alternating C–C bonds in the cyclobutadiene [C(1)–C(2) 1.495 Å, C(2)−C(3) 1.404 Å, C(3)−C(4) 1.496 Å, C(4)−C(1) 1.425 Å]. This distortion may be explained by the strong *trans*-influence of aryl and amide ligands as well as by tendency of the nickel to adopt square planar coordination environment.

Maitlis[19] has originally proposed that cyclobutadiene ligand is too labile to stabilize active metal center in catalytic cycles. For instance, platinum and palladium cyclobutadiene complexes [(C$_4$R$_4$)MCl$_2$]$_2$ can undergo nucleophilic addition of alkoxide ion even at room temperature.[20] Therefore, we explored the possible side reactions of the cyclobutadiene ligand that can disrupt the catalytic cycle shown in Scheme 1. In particular, the nucleophilic attack of acetate anion on the intermediate $\mathbf{4_{Ni}}$ was considered. It was found that nucleophilic *exo*-addition of acetate to the

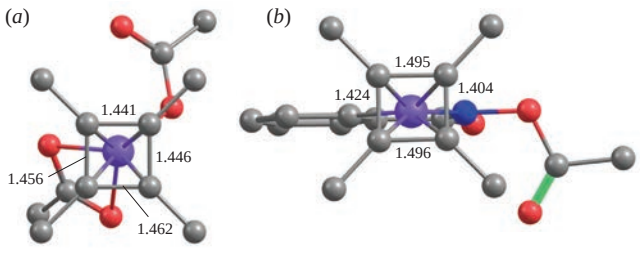


Figure 3 (*a*) The symmetrical cyclobutadiene ligand in 18-electron complex $\mathbf{1_{Ni}}$ and (*b*) the distorted one in 16-electron complex $\mathbf{4_{Ni}}$. Distances are given in Å; hydrogens are omitted for clarity.

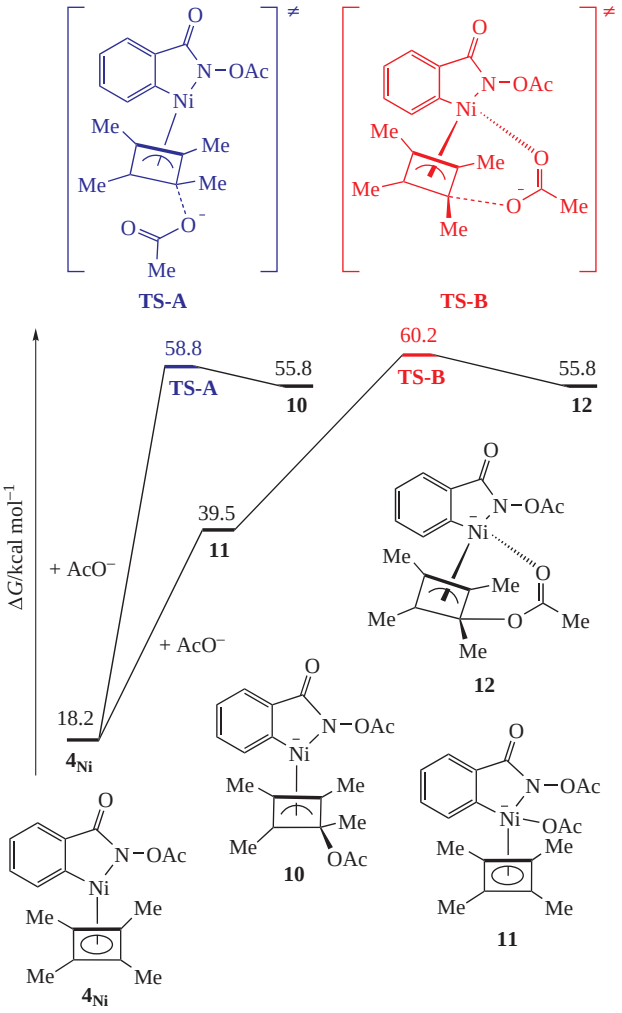


Figure 4 Possible side nucleophilic addition of AcO^- anion to intermediate $\mathbf{4_{Ni}}$.

cyclobutadiene ligand has very high activation barrier of 58.8 kcal mol^{-1} (**TS-A**, Figure 4), while the alternative pathway with preliminary coordination of acetate anion at the metal center (intermediate **11**) followed by *endo*-attack of the cyclobutadiene ligand has even higher barrier of 60.2 kcal mol^{-1} (**TS-B**). The replacement of cyclobutadiene ligand in $\mathbf{4_{Ni}}$ by acetate ion was found to proceed through thermodynamically unfavorable η^2-cyclobutadiene intermediate, which has 74.2 kcal mol^{-1} higher energy than the starting materials (see Online Supplementary Materials). Therefore, these side reactions are rather unlikely to proceed.

In conclusion, the DFT calculations revealed that cyclobutadiene nickel complexes may indeed act as catalysts for C–H activation of arenes equipped with directing groups. In particular, the activation barrier for acetate-assisted deprotonation and metalation of *N*-acetoxybenzamide by Cb*Ni(OAc)$_2$ species is 29.2 kcal mol^{-1}, suggesting that it can proceed under moderate heating (80–120 °C). At the same time, further reaction of the intermediate nickelacycle with acetylene has prohibitively high barrier of 35.6 kcal mol^{-1}. Therefore, coupling partners other than alkynes are more promising for experimental investigations. The side process of nucleophilic addition to the cyclobutadiene ligand is unlikely because of the very high energy barriers.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2019.05.007.

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